

Chapter 8. Commodity Thermoplastics and Fibers

U.S. polymer production in 1993 --- 67 billion pounds

thermoplastics : 69%, fibers : 14%

thermosets : 10%, rubbers : 7%

8.1 Thermoplastics

U.S. thermoplastics production in 1993

LDPE : 26%, PVC : 22.3%, HDPE : 21.4%, PP : 18.6%, PS : 11.7%

8.1.1 Polyolefins

Comparison of properties

TABLE 8.2 PROPERTIES OF COMMODITY POLYOLEFINS

Property	ASTM	LDPE	HDPE	PP
Specific gravity	D792	0.91-0.93	0.94-0.97	0.90-0.91
Crystallinity, %	—	50-70	80-95	82
Melt temperature, °C	—	98-120	127-135	165-171
Tensile strength, MPa ^a	D638	4.1-16	21-38	31-41
Tensile modulus, GPa ^b	D638	0.10-0.26	0.41-1.24	1.10-1.55
Elongation-to-break, %	D638	90-800	20-130	100-600
Impact strength, notched Izod, J m ⁻¹ ^c	D256	No break	27-1068	21-53
Heat-deflection temperature, °C, at 455 kPa (66 psi)	D648	38-49	60-88	225-250

^aTo convert MPa to psi, multiply by 145.

^bTo convert GPa to psi, multiply by 1.45×10^5 .

^cTo convert J m⁻¹ to lb_f in.⁻¹, divide by 53.38.

* Polyethylene(PE)

commercialized in 1939 by ICI in England (LDPE)

- LDPE

: packaging film, wire & cable insulation, moldings, coatings

Polymerization : high pressure(3000atm), 250°C

in autoclaves or continuous tubular reactors

Linear --- strength, Branched --- toughness

To impart low T flexibility, acrylates, vinyl esters & vinyl ethers may be added.

Incorporation of vinyl acetate (<7%) (i.e., modified LDPE)

--- better toughness, clarity, & gloss

Copolymers of ethylene & vinyl alcohol (EVOH)

--- better processability, moisture resistance, gas-barrier

Films from copolymers of ethylene and ethyl acrylate

--- outstanding tensile strength, elongation-to-break, clarity, resistance to stress cracking, & flexibility at low T

MW of LDPE : 6,000 - 40,000

MI(melt index) : 0.1 - 109

cf.) MI(ASTM D1238) : the weight of polymer(in grams) extruded through a standard capillary at 190°C in 10min.

Branching mechanism : (intramolecular) backbiting, intermolecular chain transfer

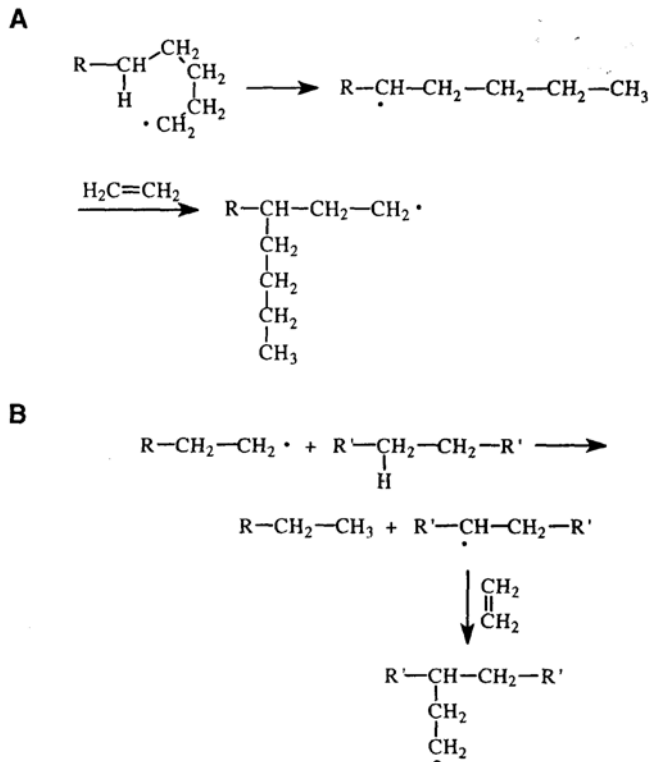


Figure 8.1. Mechanisms of branching during the free-radical polymerization of low-density polyethylene. **A.** Formation of a *n*-butyl (C₄H₉) branch by an intramolecular "back-biting" mechanism. **B.** Formation of long-chain branches via an intermolecular chain-transfer mechanism. Long alkyl end chains are represented by R and R'.

- HDPE

: bottles, containers, crates, pails, blown films

Polymerization : 100atm, 200°C by Philips type supported catalysts (CrO₃ or AlO₃),
or low pressure(1-10atm), 60-75°C by Ziegler-Natta catalysts

PE with 5 million MW --- specialty applications (ex. artificial hip replacements)

- LLDPE(by Unipol process, faster cycling time during molding than LDPE),

MDPE, VLDPE ($\rho < 0.915\text{g/cm}^3$)

* Polypropylene(PP)

: pipe, sheet, blow moldings, fibers, cases

Polymerization : 50-80°C 5-25atm by Ziegler-Natta catalysts

90% isotactic form, light weight ($\rho = 0.92\text{g/cm}^3$), high HDT

cf.) s-PP : 고무상 점탄성체, $\rho=0.85\text{g/cm}^3$, 강도 ↓, 성형용으로 부적합,

lower T_m , susceptible to solvent attack

In comparison to HDPE, higher T_m , lower crystallinity,

better crack resistance(fatigue resistance, living hinge)

Conformation : helix form (3 monomer units per a single turn)

cf.) PE : zigzag planar form

Disadvantage : susceptibility of methyl groups to thermooxidative degradation

8.1.2 Vinyl polymers

* Styrenics

Principal use for PS : packagings

Comparison of properties

TABLE 8.3 PROPERTIES OF STYRENIC POLYMERS

Property	ASTM	GP-PS	HIPS	ABS
Specific gravity	D792	1.04–1.05	1.03–1.06	1.03–1.58
Tensile strength, MPa ^a	D638	36.6–54.5	22.1–33.8	41.4–51.7
Tensile modulus, GPa ^b	D638	2.41–3.38	1.79–3.24	2.07–2.76
Elongation-to-break, %	D638	1–2	13–50	5–25
Impact strength, notched Izod, J m ⁻¹ ^c	D256	13.3–21.4	26.7–587	160–320
Heat-deflection temperature, °C at 455 kPa (66 psi)	D648	75–100	75–95	102–107

^a To convert MPa to psi, multiply by 145.

^b To convert GPa to psi, multiply by 1.45×10^5 .

^c To convert J m⁻¹ to lb_f in.⁻¹, divide by 53.38.

GPPS (general-purpose PS)

HIPS (high-impact PS)

ABS

AN ↑ → chemical resistance ↑, craze resistance ↑, strength ↑

BR ↑ → impact strength ↑, clarity ↓

St ↑ → rigidity ↑, processibility ↑

⇒ "taylor-made plastics"

SAN or AS

EPS (expandable PS)

flame-retardant grades -- by adding <1% of brominated aliphatic compounds

Crosslinked PS can be made by copolymerizing styrene with divinylbenzene.

Disadvantage : susceptible to photooxidative degradation --> brittleness & yellowing

degradation : initiated by phenyl groups (UV absorption from sunlight)

transferred to other sites along the polymer chain

resulted in bond cleavage, radical formation, and rxn with O₂

* Poly(vinyl chloride) (PVC)

rigid grade : sheet, pipe, window profiles, molded parts

flexible grade : wire coating, upholstery, floor coverings, film, tubing

(See Table 8.4)

TABLE 8.4 REPRESENTATIVE PROPERTIES OF COMMERCIAL GRADES OF PVC

Property	ASTM	Rigid	Flexible
Specific gravity	D792	1.03-1.58	1.16-1.35
Tensile strength, MPa ^a	D638	41.4-51.7	22.1-33.8
Tensile modulus, GPa ^b	D638	2.41-4.14	1.79-3.24
Elongation-to-break, %	D638	2-80	13-50
Impact strength, notched Izod, J m ⁻¹ c	D256	21.4-1068	26.7-587
Heat-deflection temperature, °C at 455 kPa (66 psi)	D648	57-82	75-95

^a To convert MPa to psi, multiply by 145.

^b To convert GPa to psi, multiply by 1.45 x 10⁵.

^c To convert J m⁻¹ to lb_f in.⁻¹, divide by 53.38.

Clear, moderately tough, low-crystallinity ($T_g = 87^\circ\text{C}$, $T_m = 212^\circ\text{C}$),

MW : 25,000 - 150,000

transparent, hard, brittle, gas barrier, water resistance, electric insulation

중합온도 : 50°C 근처, 온도가 높으면 branching 문제 및 dehydrohalogenation에 의해 HCl이 생성되고 이것이 더욱 dehydrohalogenation 촉진, 결국 물성을 deterioration

==> Thermal stability is improved by adding organo-tin and other compounds.

Chlorinated PVC (CPVC) ==> increase in HDT for hot-water pipe

Flexible film <== copolymerizing VCM with vinylidene chloride or vinyl acetate

Toughness improvement <== blending with high-impact resins (ABS, MBS)

문제점 : PVC 자체는 무독성, 잔류 VCM이 문제 --> 폐암의 유발,

소각시 HCl gas 발생 --> 소각로 수명 단축

surfactants & additives도 문제

* Poly(methyl methacrylate) (PMMA)

: moderate T_g (105°C) highly transparent, good weatherability, acid resistant

Applications : automotive industry(lamps), lighting signals, hard contact lenses, ...

optical fibers (근거리용), 석영계 fiber (장거리용, 광에너지의 손실 적음)

단점 : acetone에 용해되기 쉬움, 표면강도가 약함

Anionic polymerization at low T ==>

highly isotactic PMMA : $T_g = 45^\circ\text{C}$, $T_m = 160^\circ\text{C}$

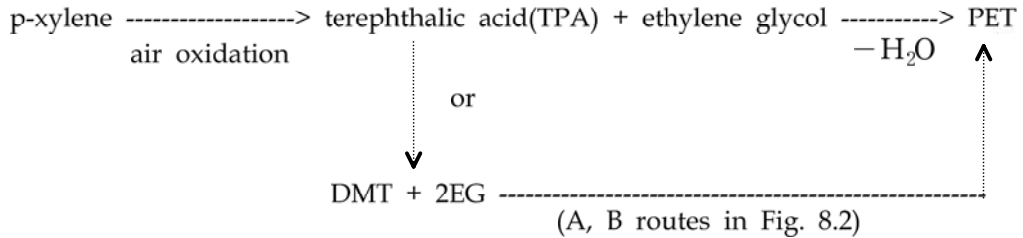
highly syndiotactic PMMA : $T_g = 115^\circ\text{C}$, $T_m = 200^\circ\text{C}$

8.1.3 Thermoplastic polyesters

Poly(ethylene terephthalate) (PET) : saturated polyesters

cf.) unsaturated polyesters --> thermosets (network polymers, 복합재료용 matrix)

Polymerization of PET :



A route : oligomeric product (n=1-4)

B route : high MW PET (Ethylene glycol is distilled off during polym'n)

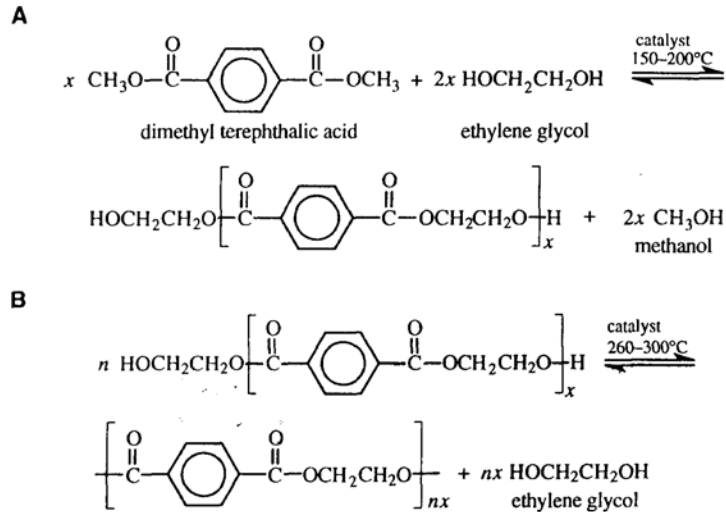


Figure 8.2. Two steps in the polymerization of poly(ethylene terephthalate). **A.** Ester interchange of dimethyl terephthalate and ethylene glycol. **B.** High-temperature esterification to yield high-molecular-weight polymer and ethylene glycol as a by-product.

용도 : fibers, soft-drink bottles, films

high recycling rate

recycled PET : used in the manufacture of insulation boards,

or thermally or chemically decomposed to its monomers

8.2 Fibers

8.2.1 Natural and synthetic fibers

* Naturally occurring fibers

Cellulose -- most abundant of all natural polymers (See Fig. 8.3)

cotton -- 94% cellulose

Principal component of animal fibers : keratin & fibroin (protein of silk filament)

(See Table 8.5)

tenacity : tensile strength of a fiber [g_t/denier] or [mN/tex]

denier : a measure of fiber thickness [g/9000m]

tex : " " [g/1000m] --> SI unit

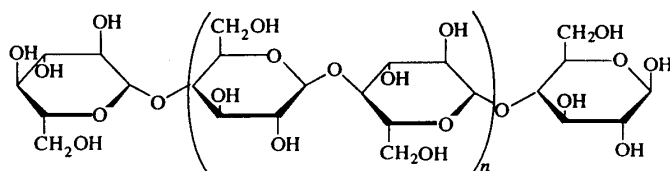


Figure 8.3. Structure of cellulose of $2n+2$ degree of polymerization.

TABLE 8.5 REPRESENTATIVE PROPERTIES OF SOME NATURAL AND SYNTHETIC FIBERS (at 65% relative humidity)

Fiber	Tenacity at Break, N/tex ^a	Extension at Break, %	Elastic Modulus, N/tex ^a	Specific Gravity
Natural Fibers				
Wool	0.09–0.15	25–35	2.2–3.1	1.30
Cotton	0.26–0.44	4–10	9–30	1.54
Cellulosics				
Cellulose ^b	0.12–0.33	10–30	3.7–5.8	1.50–1.54
Cellulose acetate ^c	0.09–0.13	25–40	2.2–3.5	1.30–1.35
Noncellulosics				
Polyester ^d	0.35–0.53	15–30	7.9	1.38
Nylon ^d	0.40–0.71	15–30	3.5	1.14
Acrylic ^d	0.40–0.44	15–20	5.3–6.2	1.17
Olefin (PP)	0.44–0.79	15–30	2.6–4.0	0.90

^a To convert N/tex to g/den, multiply by 11.3.

^b From viscose process.

^c Secondary acetate (DS less than 2.4).

^d Continuous filament.

* Synthetic fibers

: semicrystalline polymers that are capable of being spun into filaments of $L/D > 100$

Textile yarns -- produced by twisting several continuous fibers together to form a uniform structure with all filaments aligned parallel to the yarn axis

Cellulosics : derived from cellulose through chemical reaction & modification

regenerated cellulose (rayon) and cellulose acetate (acetate)

Noncellulosics : all synthetic polymers

polyester, nylon, polyolefin, and acrylic

(See Table 8.6)

TABLE 8.6 U.S. PRODUCTION OF SYNTHETIC FIBERS IN 1993

Fiber	Billions of Pounds	% of Total
Cellulosics		
Rayon	0.28	3.0
Acetate	0.23	2.5
Noncellulosics		
Polyester	3.56	38.3
Nylon	2.66	28.6
Olefin	2.14	23.0
Acrylic	0.43	4.6
TOTAL	9.30	

Source: *Chemical and Engineering News*, April 11, 1994.

8.2.2 Cellulosics

* Cellulose

--- composed of 2000 - 6000 anhydroglucose units (MW of 300,000 to 1,000,000)
 strongly hydrogen bonded and highly crystalline

==> essentially insoluble and infusible (i.e., degrades before melting)

Cellulose in fiber (rayon) or film (cellophane) by viscose process

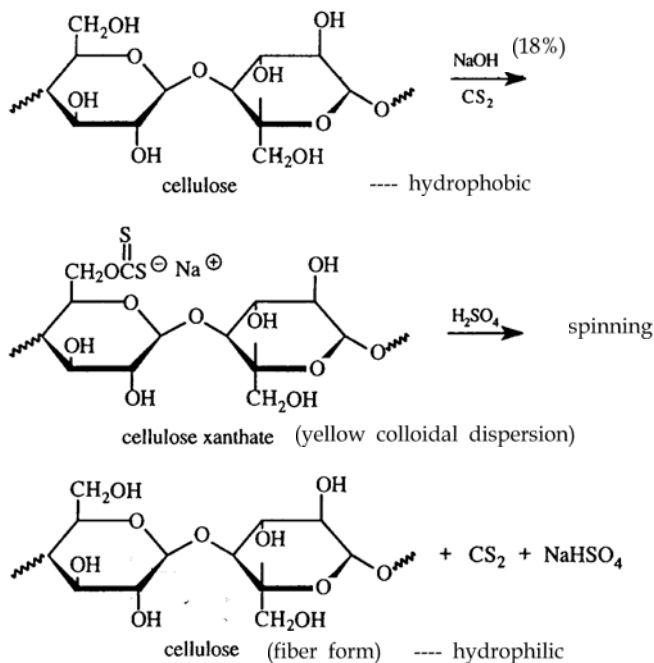


Figure 8.4. Viscose process for the production of regenerated cellulose.

Fibers obtained from regenerated cellulose

-- hydrophilic, and less developed crystalline structure than natural cellulose

* Cellulose derivatives

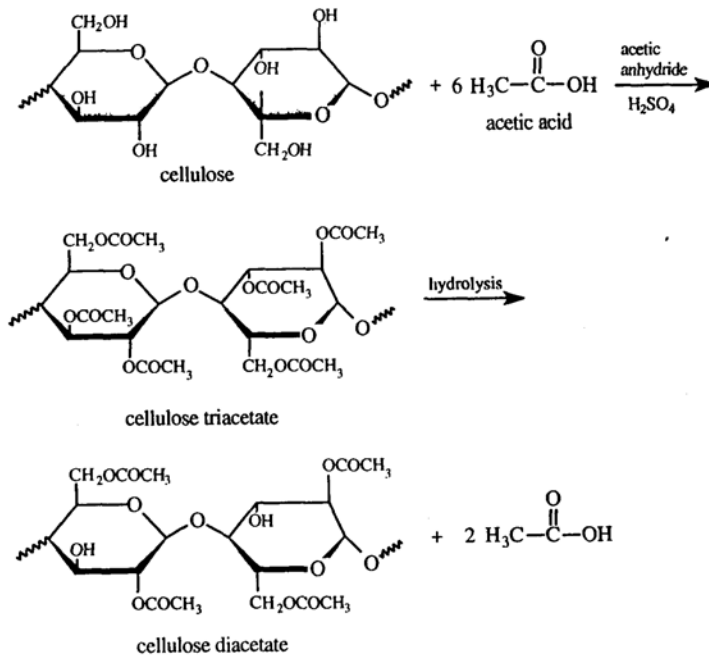


Figure 8.5. Acetylation of cellulose and partial hydrolysis of cellulose triacetate to yield cellulose diacetate.

cellulose triacetate (CTA)

- by reacting cellulose with acetic acid in acetic anhydride and sulfuric acid
- moderately crystalline, higher solubility than native cellulose
- can be wet spun

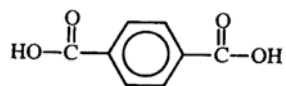
cellulose diacetate (CA)

- by hydrolyzing CTA (25-35% of acetate groups are hydrolyzed)
- can be dry spun

8.2.3 Noncellulosics

* Polyesters

Polyester fiber is defined as one composed of at least 85wt% of an ester of a dihydric alcohol(HORO₂H) and terephthalic acid(TPA) whose structure is



Poly(ethylene terephthalate) (PET) -- the largest-volume synthetic fiber commercialized by Du Pont in 1953 (Dacron[®] - fiber, Mylar[®] - film)
 low T_g (69°C), high T_m (265°C), moderate crystallinity
 resistant to many solvent & weak mineral acid,
 abrasion & oxidation resistant, good lightfastness

Dyeability -- improved by copolymerization with adipic acid & isophthalic acid
 Additives are widely used to enhance fire retardancy and antistatic properties

* Polyamides

Aliphatic polyamides ==> nylon

fiber applications, engineering plastics such as gear wheels, electrical switches & connectors, ski shoes, and automotive coolant tanks

Aromatic polyamides ==> aramids (ex., Nomex, Kevlar)

expensive, fibers for composites, substitutes for asbestos, material for tire cords

nylon-6,6 (or PA 66, poly(hexamethylene adipamide))

: by step-growth polymerization of hexamethylene diamine and adipic acid

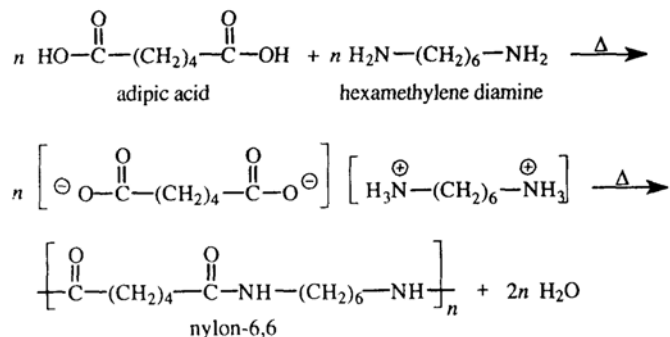


Figure 8.6. Synthesis of nylon-6,6 by means of the A-A/B-B step-growth polycondensation of adipic acid and hexamethylene diamine following an intermediate salt formation.

nylon-6 (or PA 6, poly(ε aprolactam))

: by anionic polymerization of ε aprolactam using strong bases (sodium hydride),
 or by hydrolytic polymerization of ε aprolactam

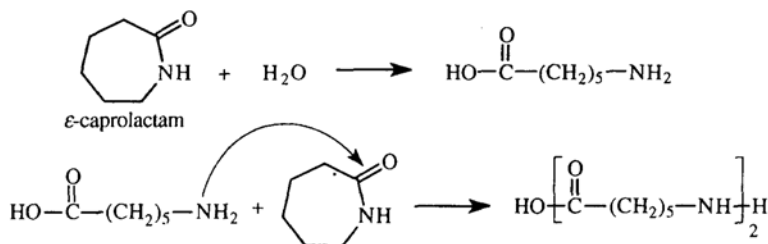


Figure 8.7. Hydrolytic polymerization of ε-caprolactam to the dimer. High-molecular-weight nylon-6 is obtained by the subsequent addition of caprolactam.

* Acrylics

Polyacrylonitrile(PAN) alone cannot be used for thermoplastic applications.

Thermoplastic and elastomeric applications can be found as a copolymer with other monomers such as styrene (e.g., ABS, SAN, and NBR).

PAN is insoluble in its own monomer ==> Polymer precipitates during bulk polym'n.

Solution polymerization in water or dimethyl formamide (DMF) with initiator ==>
dry spinning from DMF directly or wet spinning from DMF into water

Fibers are also made from copolymers with styrene, vinyl acetate, vinyl chloride,
vinylpyridine, acrylic esters, and acrylamide.

Fibers > 85% AN content ==> acrylic

35% AN content < Fibers < 85% AN content ==> modacrylic

Presence of the nitrile group(-CN) in acrylic fibers

--> strong intermolecular hydrogen-bonding --> high fiber strength

* Olefinics

Olefin fibers : Fibers > 85% of any olefin such as ethylene or propylene

Used for home furnishing(carpet and upholstery), engineering application(ropes)

Advantages of olefin fibers : low cost, light weight, resistant to solvents(hydrophobic)

Disadvantages of " : susceptibility to compressive creep and UV degradation,
difficult to dye (--> colored by pigments)

8.2.4 Fiber-spinning operations

Melt spinning : polyamide, polyester and polyolefin fibers

Solution spinning (Dry & Wet spinning) : cellulosic and acrylic fibers

* Melt spinning

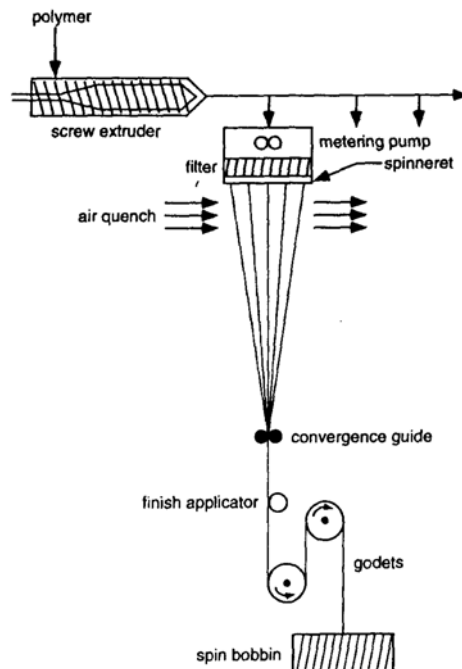


Figure 8.8. Melt spinning of synthetic polymers. (Adapted from J. E. McIntyre and M. J. Denton, in the *Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, ed., John Wiley & Sons, New York, 1990. Copyright © 1990 John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.)

Polymer is melted or extruded --> clarified by a filter --> pumped through a die (spinneret) --> extruded fiber is cooled and uniaxially stretched by take-up rollers (godets) --> wound onto a spin bobbin --> texturing and dyeing --> woven into fabric

ex.) PET : melt spun at 286°C through a spinneret containing 24 orifices having 0.5mm diameters. Average extrusion velocity : 1-20 m/min.

* Solution spinning

: typically in the range of 20 to 40 wt% of polymer concentrations

. Dry spinning (cellulose acetate and acrylics)

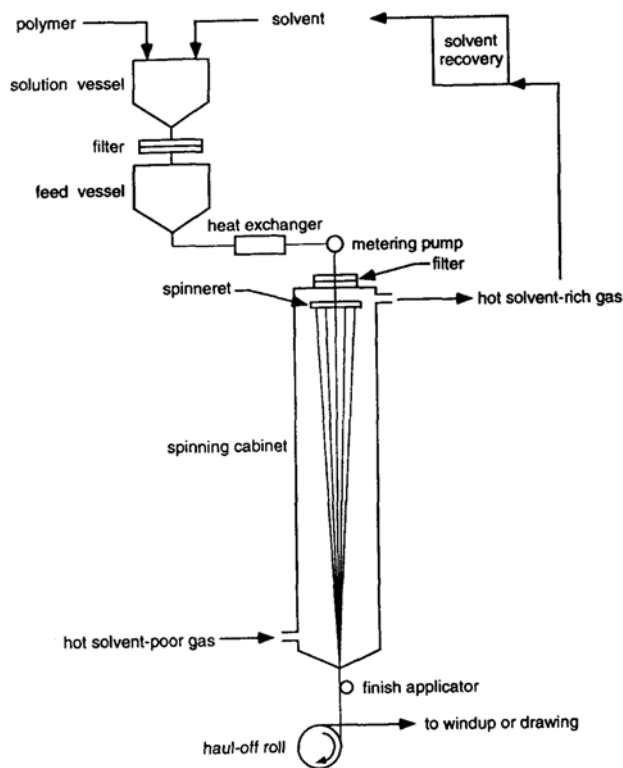


Figure 8.9. Typical process for the dry spinning of synthetic fibers. (Adapted from J. E. McIntyre and M. J. Denton, in the *Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, ed., John Wiley & Sons, New York, 1990. Copyright © 1990 John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.)

Solution is filtered --> pumped through a spinneret into a spinning cabinet (up to 25ft in length) --> heated air is passed through --> solvent evaporates into the airstream --> solvent is carried out of the cabinet for solvent recovery --> dried fiber is oriented and wound onto a bobbin

Solvents : acetone, carbon disulfide, water

Speed of a dry spinning line : up to 1,000m/min

. Wet spinning (rayon, PVA, PVC, PAN)

: Fiber formation results from the coagulation of the polymer solution by immersion in a nonsolvent such as water.

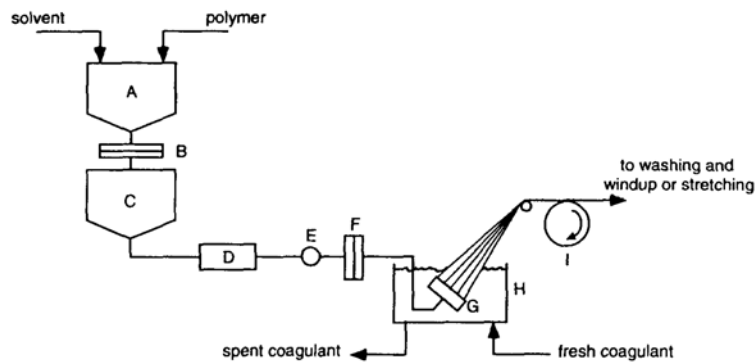


Figure 8.10. Wet-spinning process. A, solution vessel; B and F, filters; C, feed vessel; D, heat exchanger; E, metering pump; G, spinneret; H, spin bath containing coagulant; I, haul-off roll. (Adapted from J. E. McIntyre and M. J. Denton, in the *Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, ed., John Wiley & Sons, New York, 1990. Copyright © 1990 John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.)

Spinneret is directly immersed in the nonsolvent bath.

Linear velocity of a wet spinning -- much slower than either melt or dry spinning

High productivity can be obtained by spinning multiple fibers from a single spinneret

PAN -- wet spun from DMF solution into dimethylacetamide(DMAC) or

from 50% sodium thiocyanate into aqueous 10% sodium thiocyanate

Polyurethane elastomers(Spandex) -- wet spun from DMF into water

Spinning of hollow fiber membranes (for gas or liquid separation)

: Extruded fiber may first pass through air before entering the bath

(parameters : concentration of spinning solution, T, extent of air drying)

--> Asymmetric fibers (dense thin skin, thick microporous support layer)